Year 2 Update:
Investigation of Chemical Vapor Deposited Aluminum as a Replacement Coating for Cadmium

Dr. Elizabeth Berman and Dr. Eric Brooman
Air Force Research Laboratory, WPAFB, OH

Prof. Roland Levy
New Jersey Institute of Technology, Newark, NJ

Dr. Dennis Deavenport, Dr. Fernando Gomez and Mr. Sam Newberg
Akzo Nobel Company, Deer Park, TX

Mr. John H. Beatty
Army Research Laboratory, Aberdeen Proving Ground, MD

Mr. Andrew Schwartz
Naval Air Systems Command, Patuxent River, MD

Mr. Stephen Gaydos
The Boeing Company, St. Louis, MO

Joint Cadmium Alternatives Team Annual Meeting
New Orleans, LA
24 January, 2007

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE **24 JAN 2007**	2. REPORT TYPE	3. DATES COVERED **00-00-2007 to 00-00-2007**

4. TITLE AND SUBTITLE **Year 2 Update: Investigation of Chemical Vapor Deposited Aluminum as a Replacement Coating for Cadmium**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Air Force Research Laboratory,Wright Patterson AFB,OH,45433**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S) 11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
27th Replacement of Hard Chrome and Cadmium Plating Program Review Meeting, January 23-25, 2007, New Orleans, LA. Sponsored by SERDP/ESTCP.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**21**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Problem Statement

- **Cadmium provides unique combination of properties when used as a coating on weapon and support systems**
  - Ease of application, not line-of-sight limited, good adhesion and corrosion resistance, lubricity, low electrical (contact) resistance
- **However, cadmium is associated with environmental, health and safety issues**
  - Listed as a hazardous chemical
  - Emission levels set by the EPA, OSHA, various state and local agencies, as well as by Executive Orders
- **Suitable replacement needed for *high-strength* steels other than currently used Ion Vapor Deposited (IVD) or sputtered aluminum**
  - Line of sight deposition techniques
  - Vacuum requirement limits throughput and results in high cost
  - Usually require post-treatments to be effective

Technical Background

Aluminum has advantages over cadmium

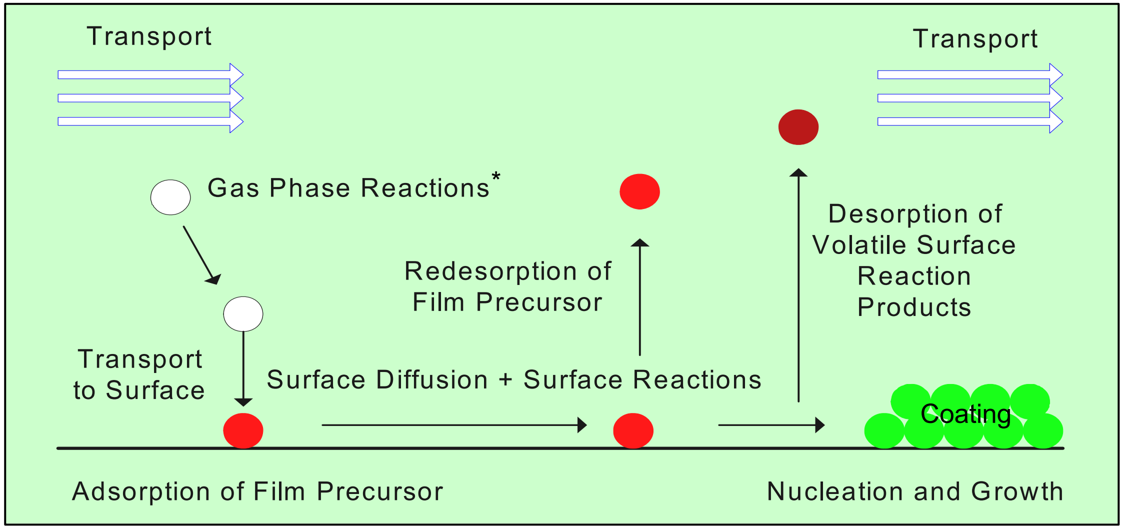
- Not a hazardous material
- Good corrosion resistance (galvanic protection)
- Good chemical resistance to aircraft fluids/chemicals
- Withstands higher operating temperatures
- Lower vapor pressure (necessary for space applications)
- Acceptable alternative under MIL-DTL-83488

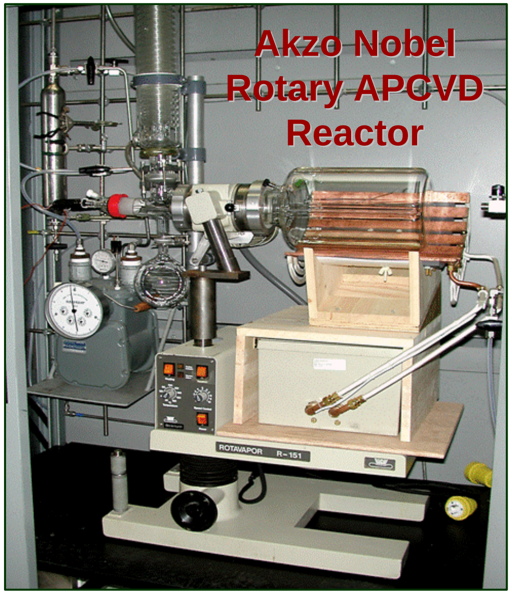
Key Technical Issues to be Addressed by APCVD Process

- **Process not involving a vacuum process preferred**
  - Less complicated equipment; higher throughput possible
- **Low processing temperature for high-strength steels**
  - Mechanical properties of substrate material must be retained
- **Avoidance of hydrogen uptake during processing**
  - No environmentally assisted cracking (e.g., H_2 embrittlement)
- **Conformal coatings of desired thickness and microstructure, compatible with substrate material**
  - Protect substrate from damage and extends useful life
- **Adherent coatings with required chemical, physical and mechanical properties**
  - Protect part/component from corrosive/erosive environments and allow required function(s) to be performed

Technical Approach

- **Coating Deposition**
  - **Precursors:** pure tri-isobutyl aluminum (TIBA); blended TIBA
  - **Carrier Gas:** nitrogen
  - **Deposition Temperatures:** 275°C, 300°C
  - **Operating Pressure:** 760 mmHg (atmospheric)
  - **Substrates:** AISI 4130 steel coupons, tubes, and fasteners





* TIBA Example: $Al(i\text{-}Bu)_3 \longrightarrow Al\downarrow + i\text{-butylene}\uparrow + 3/2H_2\uparrow$

Technical Approach

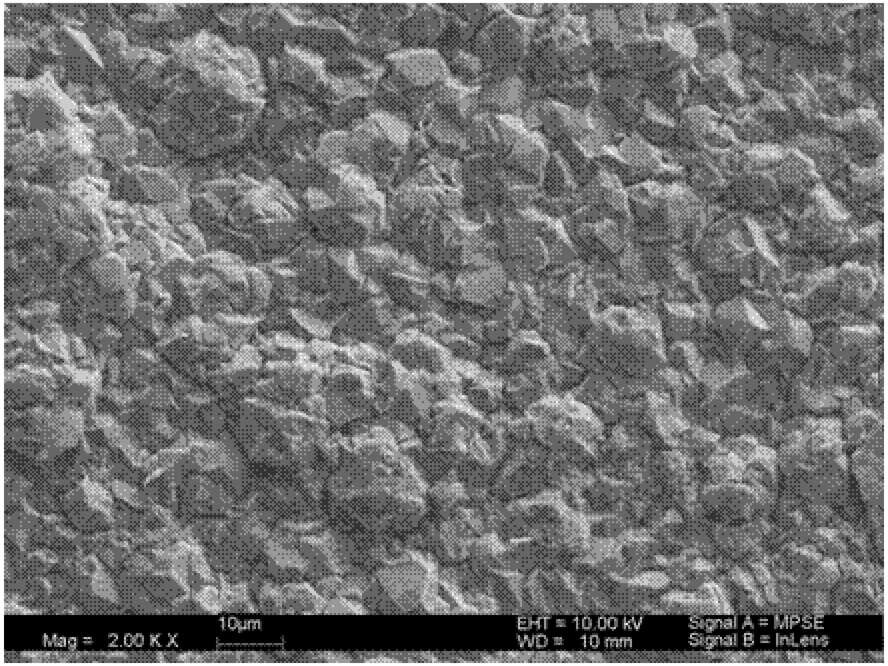
- **Year 2 Coating Characterization Testing**
  - **Appearance, Thickness, Roughness:** metallurgical mounting and sectioning, optical microscopy, scanning electron microscopy, atomic force microscopy
  - **Composition, Structure:** energy dispersive x-ray analysis, x-ray diffraction, AES, XPS, NRA
  - **Hardness, Young's Modulus:** nano-indentation calculations
  - **Adhesion:** pull off test, tape adhesion, scribed panels
  - **Electrical resistivity:** four-point probe
  - **Step Coverage:** hollow rivet sleeve with inside step
  - **Throwing Power:** Al coating deposition on open and closed tubes with 0.1875” (3/16”) and 0.3125” (5/16”) OD, 2” length, and 0.0350” wall thickness

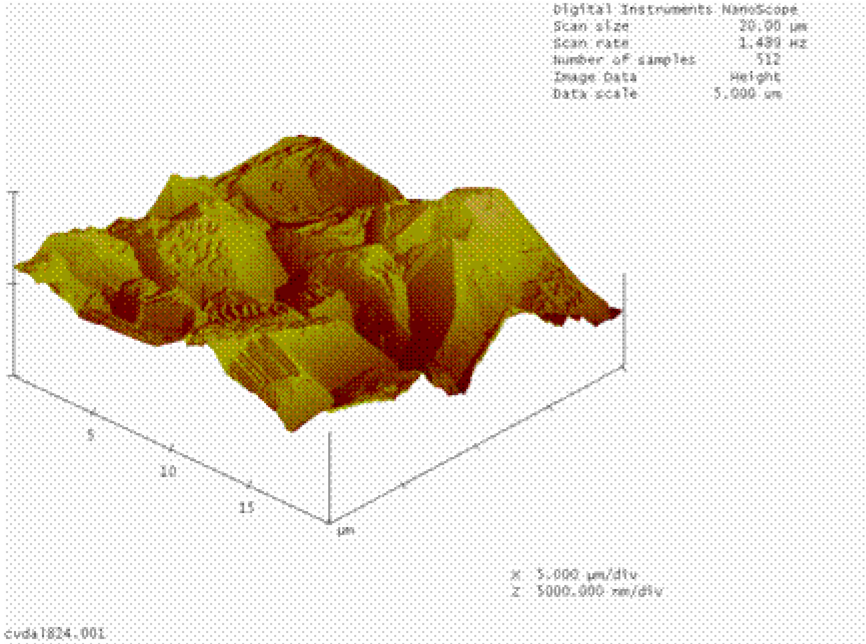
Technical Approach

- **Year 2 Coating Performance Testing**
  - **Corrosion Resistance:** ASTM B 117 Neutral Salt Fog Test; unscribed and scribed specimens, painted specimens
  - **Paint Adhesion:** ASTM D 3359 Method A
  - **Hydrogen Embrittlement**: ASTM F 519 incremental (rising) step load test
  - **Lubricity/Wear:** ASTM G 99 Coefficient of Friction, Pin-on-Disk abrasive wear
  - **Tensile Strength and Fatigue Resistance:** MIL-STD-1312

Results - Micro-Roughness

Findings: steel coupons, pure TIBA at 300°C





Roughness (RMS) = 917 nm
Film thickness = 20 um

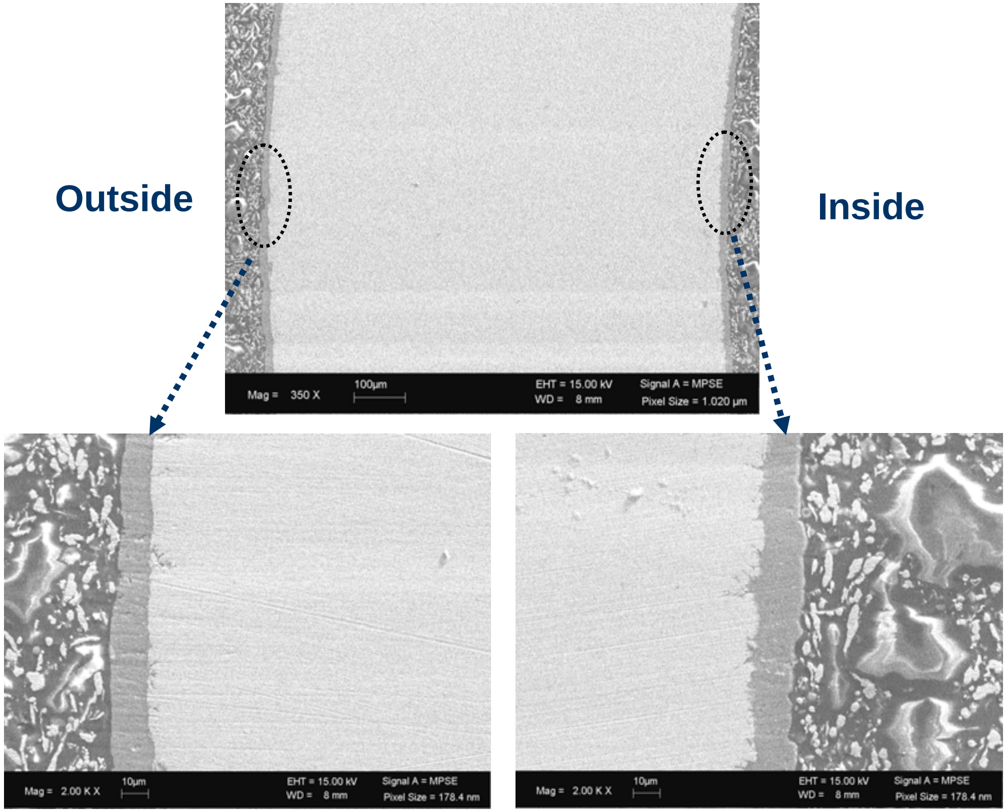
- SEM image showed dense coverage of Al coating on steel substrate
- AFM analysis of the surface showed a roughness on a **nano**-scale

Results – Throwing Power

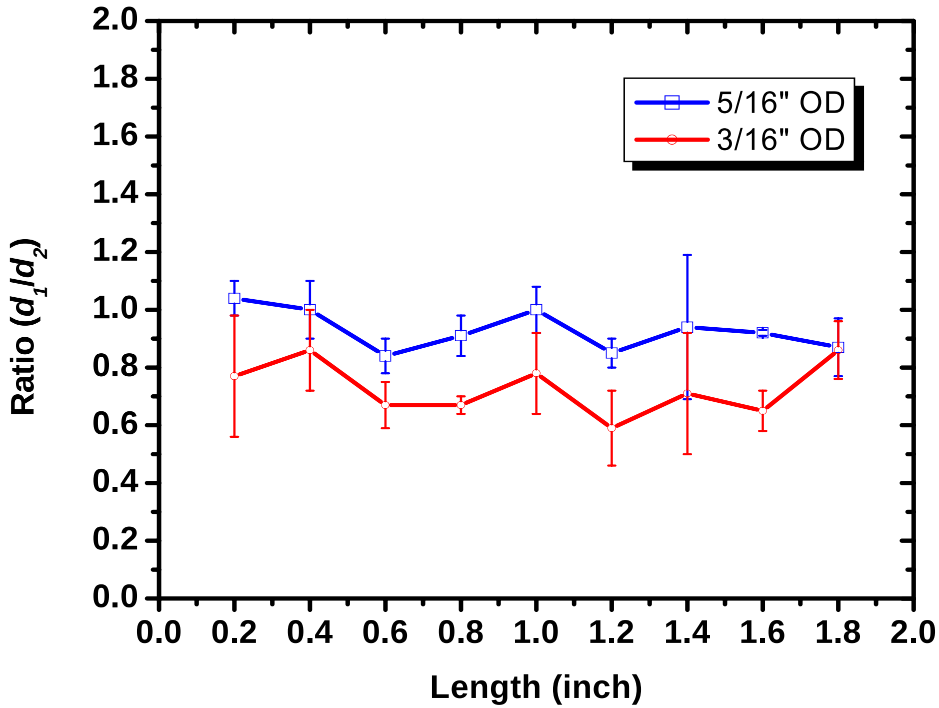
Findings: Al on outside and inside of tubes; pure TIBA at 300°C

Outside

Inside



FE-SEM image showing cross section of Al coated tube (middle point)

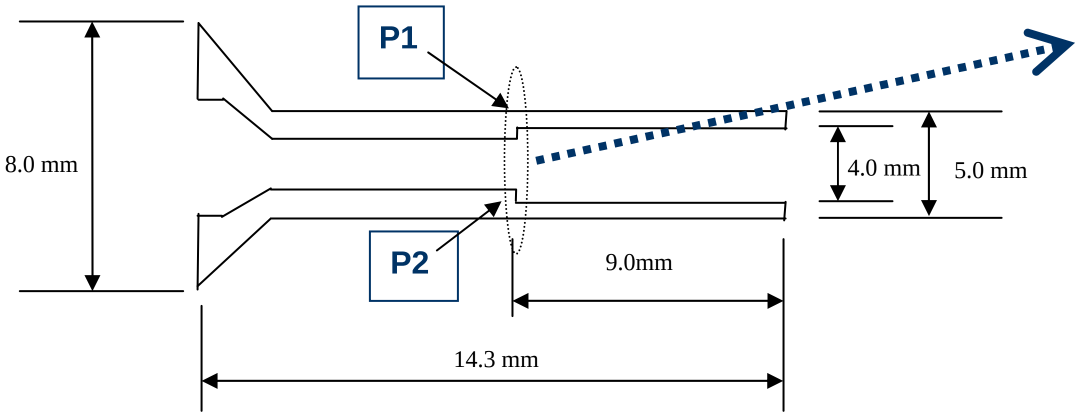


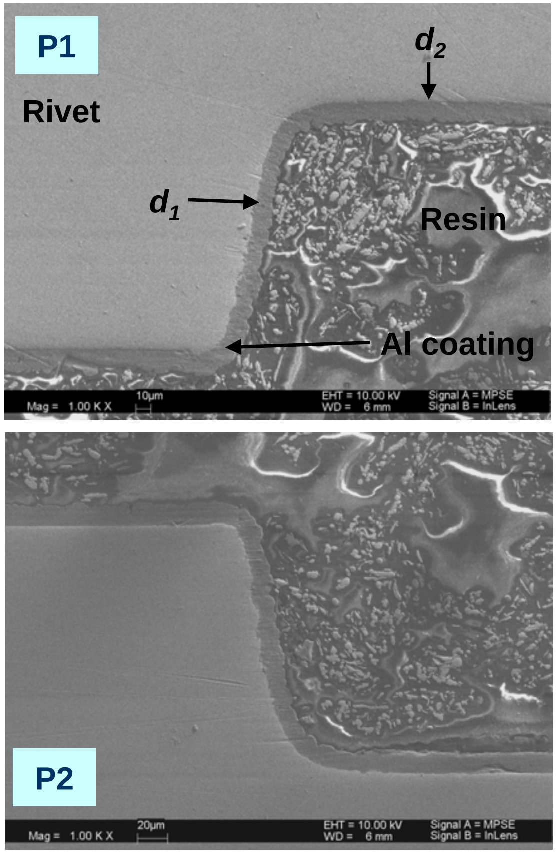
d_1 = inside coating thickness
d_2 = outside coating thickness

- **Al coatings exhibit excellent throwing power**

Results - Conformal Coverage

Findings: Al coating deposited on hollow rivet sleeve





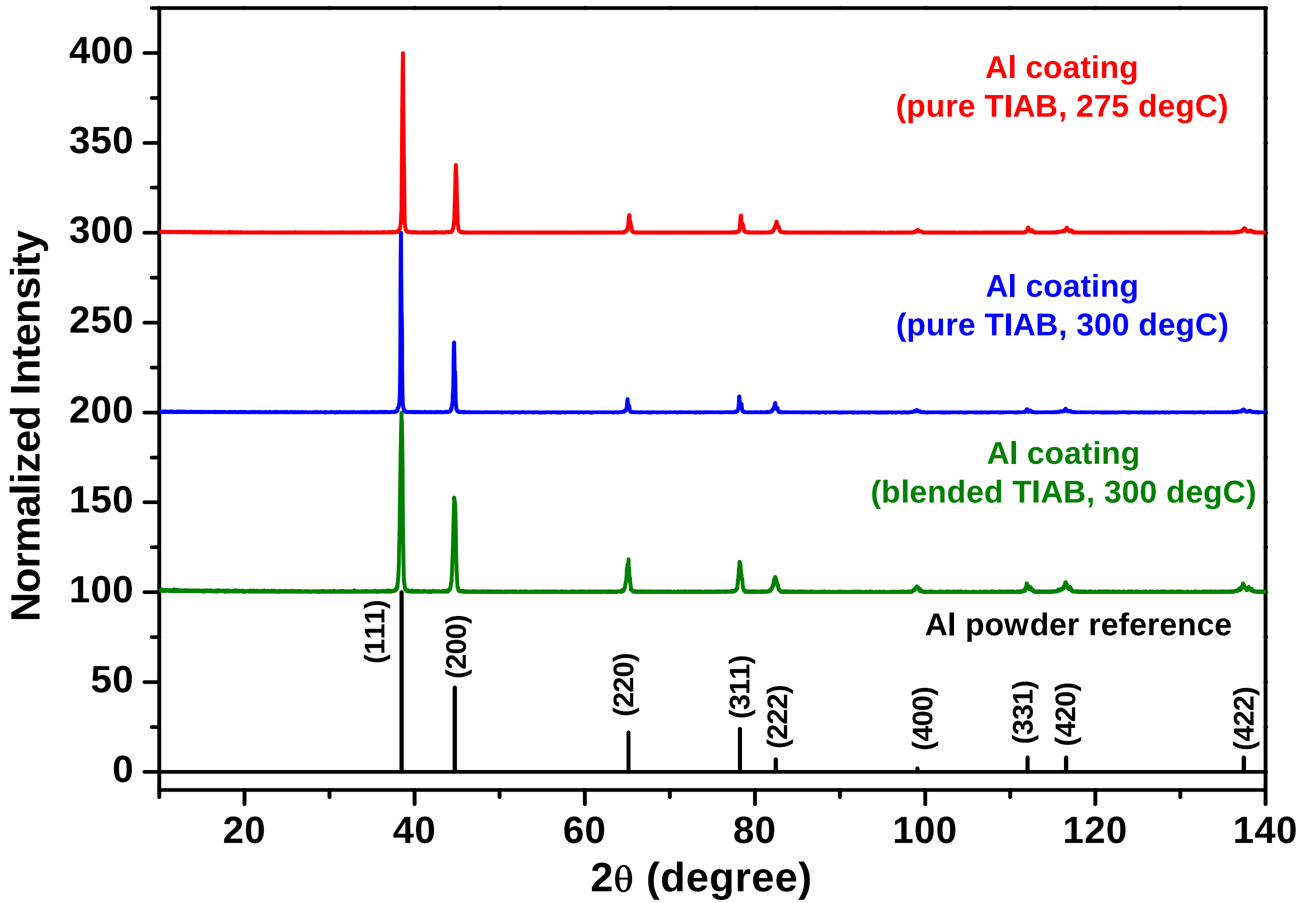
$$r = \frac{d_1}{d_2} = \frac{13.56\mu m}{14.12\mu m} = 0.96$$

[where d_1 and d_2 are average coating thickness]

- **Al coatings exhibit excellent conformal coverage (r = 0.96)**

Results - Morphology

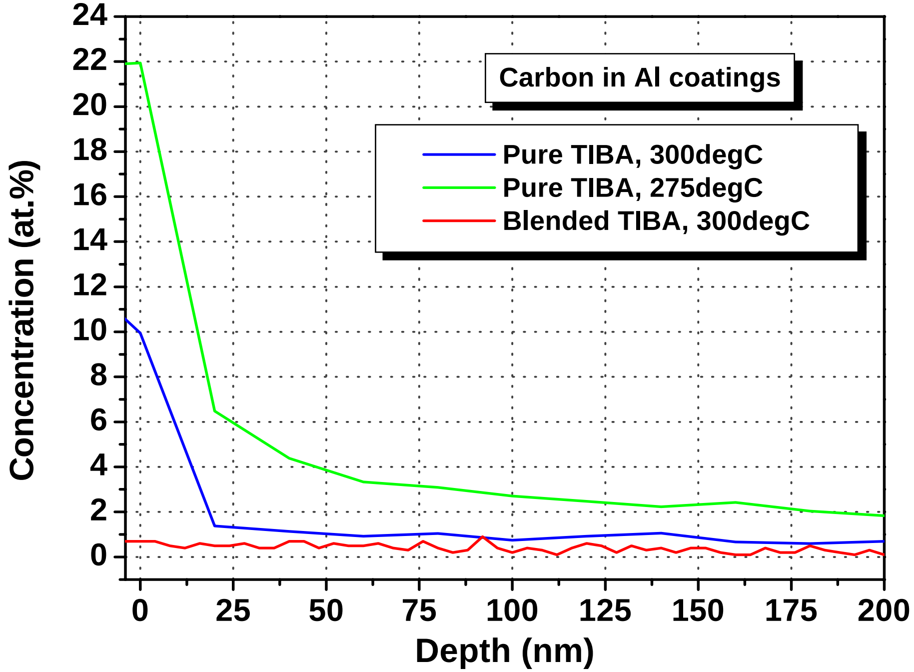
Findings: Al coatings on steel coupons

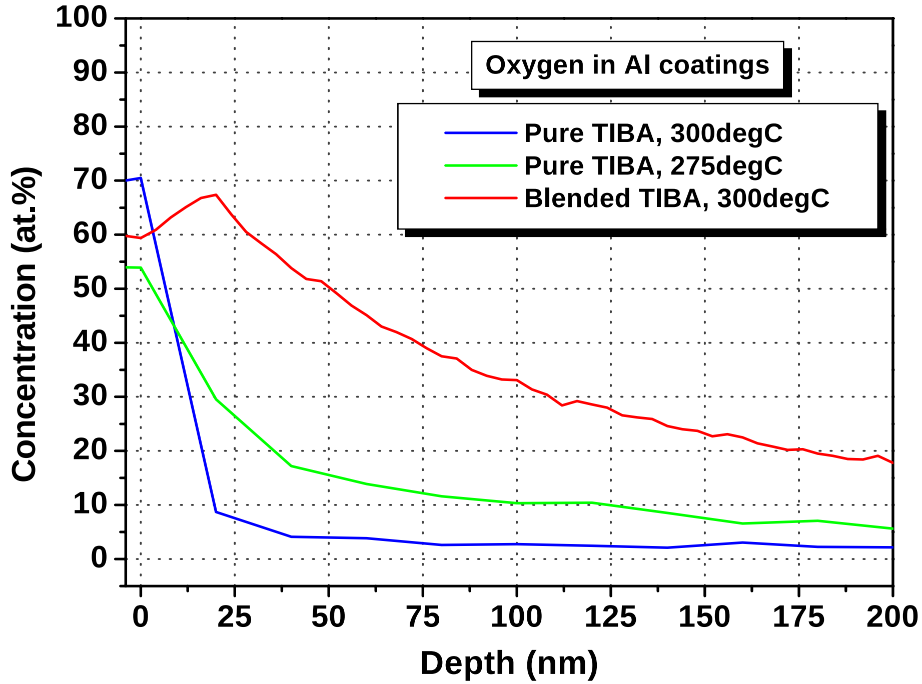


- XRD pattern - **Al coating is very similar to that of Al powder (fcc) showing polycrystalline structure with high degree of crystallinity**

Results - Composition

Findings: Steel coupons and fasteners; pure and blended TIBA

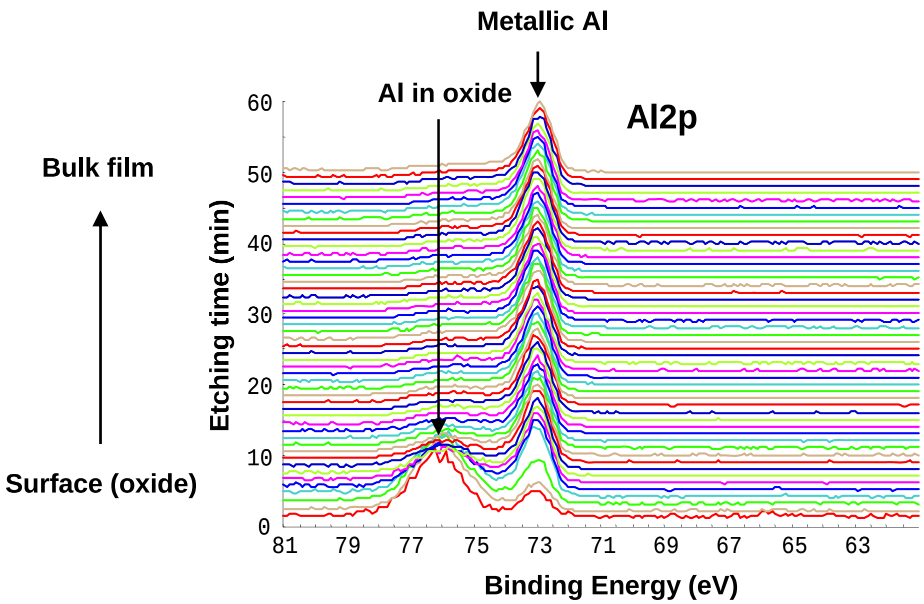


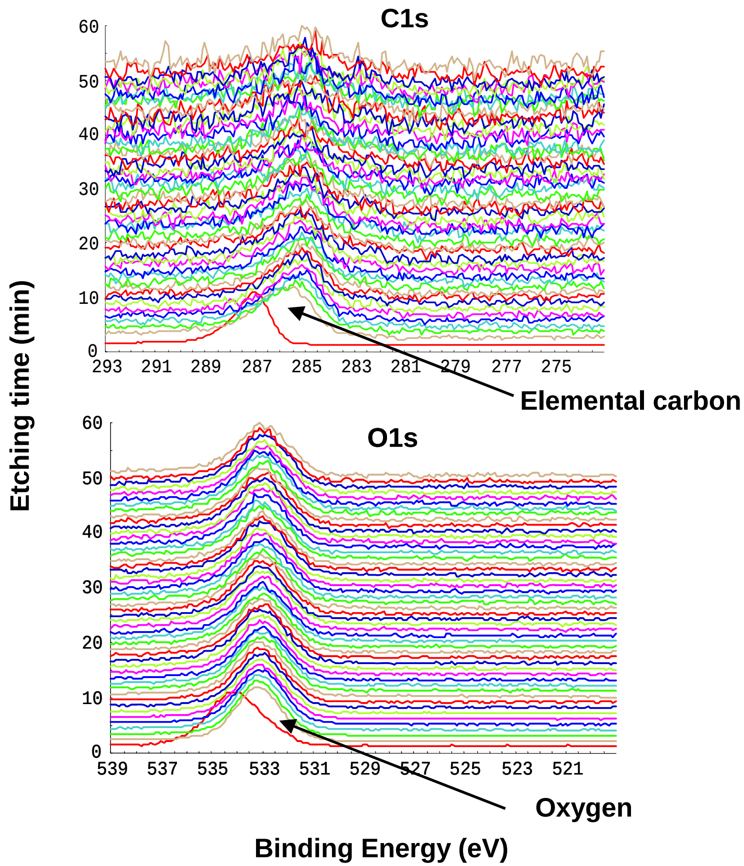


- AES Analysis Summary:
  - **C contamination in Al coatings affected by process temperature**
  - **Low C contamination observed in Al coatings using blended TIBA**
  - **Low O_2 content observed in Al coatings using pure TIBA**

Results - Composition

Findings: Steel coupons and fasteners; pure TIBA at 300°C

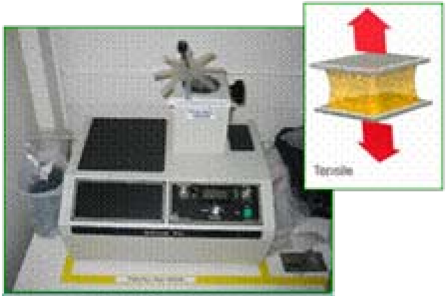




- XPS Analysis - **APCVD Al coating composition close to bulk pure Al**

Results - Physical Properties

- **Mechanical Properties:** TIBA at 300°C
  - <u>Adhesion (Pull) Test on AISI 4130</u>
    - 703±85 kg/cm^2 (pure TIBA)
    - 684±30 kg/cm^2 (blended TIBA)
  - <u>Nanoindentation Test</u>
    - Hardness is ~551 MPa
    - Young's Modulus is ~36 GPa
  - <u>Coefficient of Friction</u>
    - Greater for APCVD Al coatings than Cd coatings (as expected)
- **Electrical Resistivity:** TIBA at 300°C
    - Resistivity = 3.5 ±0.1 μohm·cm (~14.7 μm coating on Si_3N_4-coated steel sample)
    - Value close to bulk Al (2.7 μohm·cm) indicating purity of Al coating



Pull Off Test Fixture

APCVD Al Coatings Have Good and Acceptable Physical Properties

Results - Corrosion Resistance

Preliminary Salt Fog Exposure: pure TIBA at 300°C

- 1"X 2" AISI 4130 steel coupon substrate
- ASTM B 117 salt fog testing

17 days in B117 salt fog

As deposited | **Scribed as deposited** | **With TCP** | **Scribed with TCP**

- **Red rust began to form at 27 days - test discontinued**
- **Post treatment with TCP did not improve corrosion resistance**
- **TCP needs to be optimized for this coating**

APCVD Al meets Type I, Class 1 Cd Coating Requirement

Results - Corrosion Resistance

Preliminary Painted Corrosion Test: pure TIBA at 300°C

- 1" X 2" AISI 4130 steel coupons
- MIL-PRF-23377C primer and MIL-PRF-85285 topcoat
- ASTM B 117 salt fog testing

After 17 days in B117 Salt Fog

Unscribed

Scribed

- **Al painted coatings exhibit good corrosion resistance - no blistering or red rust up to 27 days - test discontinued**

Results - H_2 Embrittlement

- Preliminary tensile strength measurements
  - Al coatings deposited on notched round bars (Control - AISI 4340 bar (ultimate tensile ≈ 400 ksi))
    - *Notch tensile strength not in acceptable range*
  - H_2 relief bake after Al coating deposition
    - *Notch tensile strength in acceptable range*

- ASTM 519 rising step load method
  - Al coatings deposited on notched round bars (Control - AISI 4340 bar (ultimate tensile ≈ 400 ksi))
    - *Failed HE rising step load test*
  - H_2 relief bake after Al coating deposition
    - *Passed HE rising step load test*

Round bar

Round bar test in progress

Conclusions

- Morphological analysis by SEM and AFM revealed that the APCVD Al coatings are dense and rough, but on a nano-scale
- APCVD Al coatings exhibit excellent conformal coverage with uniform coating thickness
- APCVD Al coatings exhibit excellent / good:
  - throwing power
  - step coverage
  - adhesion
  - hardness
- Coefficient of friction of APCVD Al higher than for Cd, but still acceptable

- APCVD Al coatings exhibit face-centered cubic pattern that is identical to that of the Al powder reference (XRD)
- Compositional depth profile shows that APCVD Al coatings are oxidized on the surface but relatively pure within the bulk (AES / XPS / NRA)
- C, H_2 and O_2 impurity concentrations depend on deposition temperature and type of precursor used

Conclusions (cont.)

- Preliminary corrosion test (salt fog): APCVD Al (bare) met requirement for a Type I, Class 1 Cd coating
- Preliminary painted corrosion test (salt fog): No loss of adhesion for the exposure time used

- Tensile strength and hydrogen embrittlement tests: preliminary data promising when APCVD Al coatings receive the conventional hydrogen relief bake post treatment used for Cd

Year 3 - Way Ahead

- Further In-depth Physical Property Testing (i.e.adhesion, compatibility w/ substrate)
- Fluid / Cleaning Chemical Corrosion Resistance
- Optimization of Deposition / Processing Temperature
- Develop Plan to Scale Up APCVD Al Process

Acknowledgments

- **NJIT (Coating Characterizations)**
  - Dr. Sung Min Maeng
  - Dr. Yong Seok Suh
  - Mr. Sipeng Gu